REMARKS/ARGUMENTS:

Claims 29-42, 55-62, 64-66, and 68-70 are pending in the application and have been rejected in the Advisory Action dated December 23, 2003. Claims 29 and 64 are amended. Reexamination and reconsideration of the application, as amended, are respectfully requested.

Claim Rejection Under 35 U.S.C. § 102:

Claims 29-34, 36-38, 41-42, and 55-56 are rejected under 35 U.S.C. § 102(b) as being anticipated by Varma, U.S. Patent No. 5,622,826 (Varma). This rejection is respectfully traversed.

Applicant previously argued that Varma does not anticipate claim 29 for two reasons: (1) Varma does not teach a *modified surface* and (2) Varma does not teach the *immobilization* of a biopolymer on the modified surface *by adsorption*. With respect to the first argument, the Examiner appears to believe that Varma teaches the modified surface of the present invention because Varma recites modification of a surface with isocyanates or isothiocyanates. The Examiner stated in the Advisory Action that Varma's recitation of isocyanates and isothiocyanates reads on instant claim 29, because it recites "derivatives" of amino, carboxyl, and thiol groups. In response, applicant amended claim 29 by *deleting the term "derivatives."* The closed transition "consisting of" of the amended claim 29 limits the claim to surfaces modified only with amino, carboxyl, and thiol groups. Since isocyanate or isothiocyanate groups do not fall within any of the listed categories, they are *excluded* from the claim language. Therefore, Varma does not anticipate or suggest amended claim 29 because he does not teach or suggest a modified surface as defined in the present invention

With respect to the argument that Varma does not teach immobilization of biopolymers by adsorption, the Examiner noted that the claim language "does not exclude ... covalent binding on the modified surface" because "[i]t is unclear what reaction is involved in the 'adsorption' reaction, since the claim language does not define the phrase."

Applicants believe that the term "adsorption" is well-defined in the art. For example, McGraw-Hill Encyclopedia of Science explains (see attached Exhibit A: Brian E. Bent, "Adsorption", in AccessScience@McGraw-Hill):

> [a]dsorption is a process in which atoms or molecules move from a bulk phase (that is, solid, liquid, or gas) onto a solid or liquid surface.
> ... At the molecular level, *adsorption is due to attractive interactions between a surface and the species being adsorbed.*
> ...The extent of adsorption *depends on physical parameters* such as temperature, pressure, and concentration in the bulk phase, and the surface area of the adsorbent, as well as on *chemical parameters* such as the elemental nature of the adsorbate and the adsorbent. Low temperatures, high pressures, high surface areas, and highly reactive adsorbates or adsorbents generally favor adsorption."

It is well-known in the art that the term "adsorption" refers to a process that is fundamentally different than "covalent binding," which involves sharing of a pair of electrons by two atoms (see, for example, attached Exhibit B: Robert G. Parr, "Chemical bonding", in AccessScience@McGraw-Hill). Consistent with the above definition of adsorption, the present invention uses the term "direct adsorption" to emphasize that, in the present invention, immobilization of biopolymers occurs without any chemical linkers and, thus, without covalent binding (page 8, lines 13-18). Unlike covalent binding, which involves sharing of a pair of electrons by two atoms, direct adsorption of the present invention is believed to occur via ionic and hydrophobic interaction (page 8, lines 22-28).

Thus, applicant believes that the term "adsorption" is well-defined in view of the knowledge in the chemical art and in further view of the instant specification.

Contrary to the Examiner's belief, the claim language of the original claim 29 excludes covalent binding on the modified surface. Nevertheless, in order to expedite the prosecution of the present invention, applicant amended claim 29 by adding an explicit limitation of adsorption *"without chemical crosslinking."* Thus, amended claim 29 expressly excludes covalent binding from the scope of the claim.

Varma does not anticipate the immobilization of a biopolymer on the modified surface by adsorption as required by claim 29. Instead, Varma teaches coating substrates with a derivatizing agent comprising isocyanate or isothiocyanate (column 18, lines 16-23) and *covalent binding* of nucleic acids with reactive isocyanate or isothiocyanate moieties of the modified substrate (column 2, lines 55-56; column 6, lines 61-62; column 19, lines 29-36). In Varma, biopolymers chemically react with isocyanate or isothiocyanate. As a result, the biopolymers are immobilized on the substrate by *chemical cross-linking* and not by adsorption as in the present invention.

As explained in the previous response, Varma doesn't make the present invention obvious. It is a discovery of the present invention that substrates with the modified surfaces, such as plasma-aminated polypropylene and polysterene substrates, are capable of direct and *stable adsorption* of biopolymers without the need for chemical linkers and covalent binding. Consequently, the present invention provides a number of advantages over the conventional methods. The advantages include, for example, a simplification of the production of polypeptide arrays and a decrease in their manufacturing costs (page 5, lines 25-30).

Varma teaches a two-step immobilization of nucleic acids on aminated polypropylene substrates. The first step includes *modification of aminated polypropylene by reaction with isocyanate or an isothiocyanate* to obtain an activated surface. The second step is a *covalent binding* of a nucleic acid

derivatized to contain an amino group with the reactive groups on the activated surface (column 3, lines 23-34; column 18, lines 7-25). These teachings of Varma demonstrate that, prior to the present invention, those skilled in the art did not expect that biopolymers could be immobilized directly on aminated polypropylene substrates by adsorption and without the need for reactive groups such as isocyanates or isothiocyanates.

Thus, based on the teachings of Varma and without the hindsight of the present invention, those skilled in the art would not have realized that substrates with a modified surface having a functionality selected from a group consisting of an amino group, a carboxyl group, and a thiol group can be used without further derivatization for the immobilization of biopolymers. Therefore, Varma does not anticipate or make present claim 29 obvious. Claims 30-34, 36-38, 41-42, and 55-56 depend from claim 29, directly or indirectly, and are patentable over Varma for at least the same reasons as claim 29.

Claims 64-66 and 68 are rejected under 35 U.S.C. § 102(b) as being anticipated by Fareed et al., U.S. Patent No. 4,970,144 (Fareed). This rejection is respectfully traversed.

Applicant previously argued that Fareed does not anticipate claim 29 because (1) he does not teach a *modified surface* and (2) because he does not teach immobilization by *adsorption without additional fixing steps*. In the Advisory Action, the Examiner stated that Fareed anticipates claims 64-66 and 68 because he teaches "*covalent bonding via an amide or ester linkage* or by adsorption."

However, as explained above, the term "adsorption" recited in claim 64 refers to a process that is fundamentally different from a covalent binding. Nevertheless, in order to expedite the prosecution of the present invention, applicant amended claim 64 by adding an explicit limitation that requires adsorption occurring "*without chemical crosslinking*," and, thus, without covalent binding.

Therefore, amended claim 64 expressly excludes covalent binding from the scope of the claim. Fareed, at best, describes covalent bonding on a modified surface, but nothing in Fareed teaches or suggests adsorption on a modified surface as required by the instant claim 64.

With respect to the applicant's argument that Fareed does not teach the language "without additional fixing steps," the Examiner did not provide any comments in the Advisory Action. However, in the Final Office Action dated August 8, 2003, the Examiner noted that the phrase "without additional fixing steps" is not defined in the specification. Accordingly, the Examiner interpreted this limitation as "any steps to immobilize biopolymer on the modified surface."

As discussed in detail in the previous responses, the limitation "without additional fixing steps" is supported by the specification as read in view of the knowledge of those skilled in the art. The limitation refers to the *stable immobilization* of biopolymers on the substrate by direct adsorption *without chemical crosslinking*, which *does not require additional treatment*, such as fixing of biopolymers. Although applicant believes that the limitation "without additional fixing steps" distinguishes the instant claim 64 from Fareed, in order to expedite the prosecution of the instant invention, claim 64 has been amended to include the step of "washing the probe assay article or the target assay article to remove loosely bound probe or target biopolymers, respectively, wherein the *washing is conducted immediately after the drying step* is completed." The support for this limitation can be found in Example 1, page 16, lines 14-19 and Example 2, page 17, lines 27-32. This limitation was added to further distinguish the instant claim 64 from Fareed.

Fareed does not anticipate instant claim 64 because he does not teach such a washing step. Instead, as discussed in the previous response, Fareed teaches "typical ELISA assay" conducted with conventional microtiter dishes (column 11,

lines 34-43). In a "typical ELISA assay," a protein is not immobilized by drying followed by immediate washing as in the present invention, but rather chemically fixed onto the dish (see step 3 of the ELISA procedure in columns 13-14 of Fareed, which requires "fixing" protein with methanol prior to the washing step).

Fareed does not suggest immobilization of polypeptides by drying. At most, Fareed teaches a conventional ELISA assay with a two-step immobilization of protein. The first step involves an overnight drying of 50 µl of the protein solution in the wells of a conventional microplate and the second step involves the immobilization of protein by "filling the wells with absolute methanol to fix the protein onto the dish" (column 14, lines 1-2). *It is only after the protein is fixed with methanol, the plates are washed with water* (column 14, line 3). Based on such teaching, those skilled in the art would have not been motivated to omit the protein-fixing step of the standard ELISA protocol without the hindsight of the present invention.

Therefore, Fareed does not teach or suggest the immobilization of polypeptides by drying on modified substrates with a washing step following immediately after the drying step and, thus, does not anticipate or make present claim 64 obvious. Claims 65-66 and 68 depend from claim 64, directly or indirectly, and are patentable over Fareed for at least the same reasons as claim 64.

Claim Rejection Under 35 U.S.C. § 103:

Claims 39-40 are rejected under 35 U.S.C. § 103(a) as being unpatentable over Varma in view of U.S. Patent No. 6,197,501 (Cremer). This rejection is respectfully traversed.

As discussed above, claim 29 is patentable over Varma. Cremer does not remedy the defects of Varma and is not relied upon by the Examiner for such. The Examiner cites Cremer for the teaching of fluorescence labeling and using a CCD

camera. Cremer does not teach or suggest adsorption of a biopolymer on a modified surface, which is obtained by introducing a functionality selected from a group consisting of an amino group, a carboxyl group, and a thiol group. Therefore, claim 29 is patentable over Varma in view of Cremer. Claims 39-40 depend from claim 29 and are patentable over the cited references for at least the same reasons as claim 29.

Claim 35 is rejected under 35 U.S.C. § 103(a) as being unpatentable over Varma in view of U.S. Patent No. 6,013,789 (Rampal). This rejection is respectfully traversed.

As discussed above, claim 29 is patentable over Varma. Rampal does not remedy the defects of Varma and is not relied upon by the Examiner for such. The Examiner cites Rampal for the teaching of ELF. Therefore, claim 29 is patentable over Varma in view of Rampal. Claim 35 depends from claim 29 and is patentable over the cited references for at least the same reasons as claim 29.

Claims 57-62 are rejected under 35 U.S.C. § 103(a) as being unpatentable over Varma and claims 68-70 are rejected under 35 U.S.C. § 103(a) as being unpatentable over Fareed. This rejection is respectfully traversed.

As discussed above, independent claim 29 is patentable over Varma and independent claim 64 is patentable over Fareed. Claims 57-62 depend from claim 29 and are patentable over Varma for at least the same reasons as claim 29. Claims 68-70 depend from claim 64 and are patentable over Fareed for at least the same reasons as claim 64.

In view of the foregoing, it is respectfully submitted that the application is in condition for allowance. Reexamination and reconsideration of the application, as amended, are requested.

If for any reason the Examiner finds the application other than in condition for allowance, the Examiner is requested to call the undersigned attorney at the Los

Angeles, California telephone number (213) 337-6700 to discuss the steps necessary for placing the application in condition for allowance.

If there are any fees due in connection with the filing of this response, please charge the fees to our Deposit Account No. 50-1314.

Respectfully submitted,

HOGAN & HARTSON L.L.P.

Dated: February 3, 2004   By:

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Exhibit A

≫ **Chemistry:** ≫ **Physical chemistry**

Adsorption

A process in which atoms or molecules move from a bulk phase (that is, solid, liquid, or gas) onto a solid or liquid surface. An example is purification by adsorption where impurities are filtered from liquids or gases by their adsorption onto the surface of a high-surface-area solid such as activated charcoal. Other examples include the segregation of surfactant molecules to the surface of a liquid, the bonding of reactant molecules to the solid surface of a heterogeneous catalyst, and the migration of ions to the surface of a charged electrode.

Adsorption is to be distinguished from absorption, a process in which atoms or molecules move into the bulk of a porous material, such as the absorption of water by a sponge. Sorption is a more general term that includes both adsorption and absorption. Desorption refers to the reverse of adsorption, and is a process in which molecules adsorbed on a surface are transferred back into a bulk phase. The term adsorption is most often used in the context of solid surfaces in contact with liquids and gases. Molecules that have been adsorbed onto solid surfaces are referred to generically as adsorbates, and the surface to which they are adsorbed as the substrate or adsorbent. See also: <u>Absorption</u>

Process

At the molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed. The magnitude of these interactions covers approximately two orders of magnitude (8-800 kilojoules/mole), similar to the range of interactions found between atoms and molecules in bulk phases. Traditionally, adsorption is classified according to the magnitude of the adsorption forces. Weak interactions (<40 kJ/mol) analogous to those between molecules in liquids give rise to what is called physical adsorption or physisorption. Strong interactions (>40 kJ/mol) similar to those found between atoms within a molecule (for example, covalent bonds) give rise to chemical adsorption or chemisorption. In physisorption the adsorbed molecule remains intact, but in chemisorption the molecule can be broken into fragments on the surface, in which case the process is called dissociative chemisorption.

The extent of adsorption depends on physical parameters such as temperature, pressure, and concentration in the bulk phase, and the surface area of the adsorbent, as well as on chemical parameters such as the elemental nature of the adsorbate and the adsorbent. Low temperatures, high pressures, high surface areas, and highly reactive adsorbates or adsorbents generally favor adsorption.

A thermodynamic description of adsorption quantifies the driving force for adsorption in terms of these parameters. An important quantity that can be defined in this regard is the Gibbs free energy of the surface, that is, the surface free energy. For a one-component system, surface free energy is also called surface tension, and it corresponds to the so-called reversible work required to create a surface. Surface free energy is the two-dimensional analog of pressure, and whereas pressure is measured as force per unit area, surface free energy is given as force per unit length. Common units for surface free energy are dynes/cm or, equivalently, ergs/cm2. Easily created surfaces such as those for liquids and layered solids (for example, graphite and mica) have low surface free energies of 0-500 ergs/cm2. Clean surfaces of tough, refractory materials have high free energies of up to several thousand ergs per square centimeter. At constant temperature and pressure, spontaneous processes lower the free energy of a system, and adsorption generally lowers the free energy of a surface; therefore, adsorption tends to occur most readily on materials with high surface free energies.

A common way to portray the results of adsorption studies on solid surfaces is in the form of an adsorption isotherm. Such a diagram gives the amount of adsorbed material per surface area at a constant temperature as a function of pressure or concentration in the bulk phase. Adsorption often initially increases with pressure and then saturates at a value that corresponds to one layer (a monolayer) of adsorbed molecules. The adsorbed monolayer has a lower free energy than the clean surface, so the driving force for adsorption is decreased upon completion of the monolayer. At still higher pressures, however, the free energy of the molecules in the gas is high enough that there is

measurable adsorption of molecules on top of the monolayer and multiple layers or multilayers can be condensed onto the surface.

An adsorption isotherm represents a chemical equilibrium in which molecules are simultaneously adsorbing to and desorbing from the surface. The isotherm shows the extent of the adsorbed layer that is the net result of these two competing processes. For many adsorption systems, particularly those involving physical adsorption, the potential energy decreases monotonically to a minimum as the adsorbate approaches the surface so that there is no energy barrier for adsorption, and equilibrium is readily achieved. Other systems involve activated adsorption, and the adsorbate encounters a potential energy barrier as it approaches the surface. This phenomenon is commonly encountered in dissociative chemisorption; the process can be depicted schematically in a one-dimensional potential diagram (Fig. 1). The height of the potential energy barrier in such a system is determined by the extent to which the molecular fragments bond to the surface as the bond within the molecule is being broken. See also: Chemical thermodynamics

Fig. 1   One-dimensional potential energy curves typical for hydrogen molecules (H_2) and atoms (H) as they approach the surface of a metal substrate. The solid curve, which involves a crossing from the molecular curve to the atomic curve, shows the type of potential profile expected for dissociative chemisorption of H_2 on the surface.
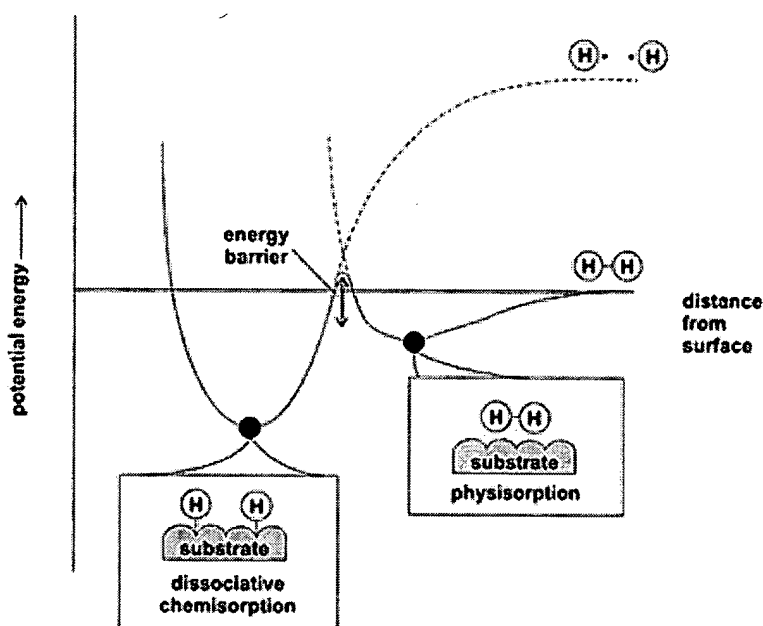
Detection and study

Studying adsorption, particularly in the monolayer regime, is difficult because of the small numbers of molecules involved. For 1 cm2 of surface area, the number of surface atoms or adsorbed molecules in a monolayer is of the order of 1015, which is only ~ 10-9 mole. Often, however, adsorbents have surface areas of hundreds of square centimeters per gram, and adsorption can be quantified simply by measuring the change in pressure or concentration of the bulk phase. Adsorption can also be quantified by measuring the change in mass of the adsorbent and by monitoring changes in the properties of the surface of the adsorbent such as the surface tension and the surface potential. By determining the number of molecules in an adsorbed monolayer, constructing an isotherm, and knowing the size of the adsorbed molecule, the area of the surface can be determined. Such a procedure is the basis for the Brunauer-Emmett-Teller (BET) method for determining surface areas.

Spectroscopies are commonly employed to study directly the structure and bonding of atoms or molecules in adsorbed monolayers. Spectroscopies that measure the absorption of light have the advantage of high resolution but the disadvantage of a low absorption cross section. High-intensity light sources (lasers and synchrotrons) and high-sensitivity detectors are often required to compensate for low absorption cross sections. If, however, the adsorbent does not interact strongly with the light, optical spectra of adsorbates can be obtained by using high-surface-area adsorbents.

Higher-sensitivity detection of adsorbed monolayers can be achieved by using electrons, ions, and atoms as probes. An advantage of these techniques is that because the probing particles do not

significantly penetrate the solid, the information that they provide is surface-specific. Interactions of the probing particles with gas phase and liquid molecules, however, limit these types of studies to vacuum conditions where the particles can be scattered from adsorbed monolayers without interference from the gas phase. See also: Monomolecular film

The application of spectroscopies to study adsorbed monolayers has formed the basis for what is known as surface science. A wide variety of spectroscopic and diffraction techniques that utilize various combinations of electrons, photons, atoms, and ions as probes have been developed as part of surface science. These include Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS), ion scattering spectroscopy (ISS), and electron or atom diffraction. See also: Auger effect; Electron diffraction; Spectroscopy; X-ray spectrometry

Another vacuum-based technique that is frequently applied to probe the strength of surface-adsorbate bonds and to study chemical reactions in adsorbed monolayers is temperature-programmed desorption (TPD). In a temperature-programmed desorption experiment, a substrate covered with an adsorbed monolayer is heated, and the species that desorb from the surface are detected (typically with a mass spectrometer) as a function of surface temperature. The resulting temperature-programmed desorption spectrum consists of peaks that are proportional to the amount of material desorbed, and the peak temperatures are related to the strengths of the adsorbate-surface bonds—higher temperatures corresponding to stronger bonds. If a reaction occurs in the adsorbed monolayer during heating, a temperature-programmed desorption spectrum shows the products that are evolved from the surface and indicates the rate at which they are produced.

Many surface science studies are carried out under ultrahigh-vacuum conditions (pressure = $10-8$ to $10-11$ torr, or $10-3$ to $10-6$ pascal). Ultrahigh-vacuum conditions make it possible to prepare and maintain atomically clean surfaces of materials that react with air. Often in these studies, samples of single crystals are utilized, and surfaces that are atomically smooth over the range of thousands of atoms can be prepared. These well-defined surfaces can serve as model systems for understanding the molecular details of adsorption.

A general finding from surface science studies of adsorption on single crystal surfaces is that, even for strongly chemisorbed layers, the adsorbate bonding to the surface is directly analogous to ligand bonding in discrete molecular compounds. An example is the ethylidyne ligand (CCH_3) bound to a rhodium surface and to a molecular cobalt complex (Fig. 2). See also: Intermolecular forces

Fig. 2 Analogy between the bonding of (a) the ethylidyne ligand (CCH_3) to a rhodium (Rh) single crystal surface and (b) to a cobalt carbonyl cluster [$H_3CC(Co)_2(CO)_7$]. The bond lengths and angles, as determined by diffraction techniques, are virtually identical in the two systems.

Key:
○ hydrogen
○ carbon
○ rhodium

(a)

Key:
○ hydrogen
○ carbon
○ cobalt

(b)
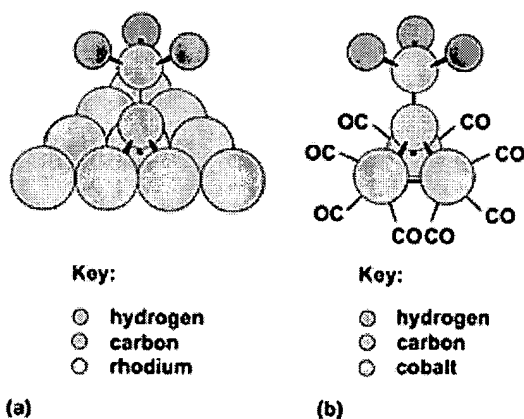
An exciting frontier in surface science studies of adsorption is the application of scanning tunneling microscopy (STM). This technique can provide an atomic resolution image of the electronic structure at the surface (Fig. 3). See also: Scanning tunneling microscope

Fig. 3 Scanning tunneling micrographs of 5✕2.25 nanometer areas of (a) the basal plane of a graphite surface and (b) the same surface after being covered with a liquid drop of 1-triacontanol. The bright spots in a correspond to every other carbon atom on the graphite surface. The lumps along the fibrous strands in b can be correlated with every other CH_2 group in the 30-carbon chain of 1-triacontanol ($C_{30}H_{61}OH$), which is adsorbed as an ordered monolayer on the graphite surface.

(Courtesy of Dr. B. Venkataraman, Dr. J. Breen, and Prof. G. W. Flynn)
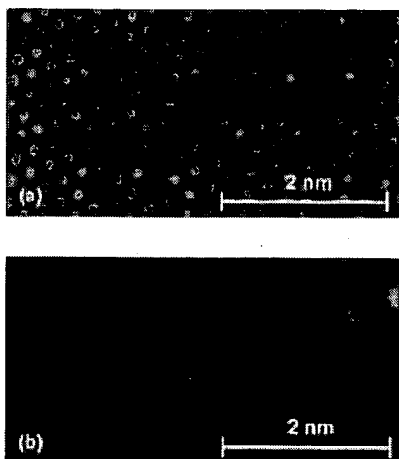
Applications

Direct applications of adsorption in processes such as filtration and detergent action are well known. Adsorption is also the basis for a series of vacuum pumps known as getter pumps. In these pumps, molecules are removed from the gas phase either by physisorption on high-surface-area materials at low temperatures (cryopumps and sorption pumps) or by chemisorption on highly reactive metal surfaces (ion pumps and titanium sublimation pumps).

Adsorption also plays an important role in processes such as heterogeneous catalysis, electrochemistry, adhesion, lubrication, and molecular recognition. In heterogeneous catalysis, gas or solution-phase molecules adsorb onto the catalyst surface, and reactions in the adsorbed monolayer lead to products which are desorbed from the surface. In electrochemistry, molecules adsorbed to the surface of an electrode donate or accept electrons from the electrode as part of oxidation or reduction reactions. In adhesion and lubrication, the chemical and mechanical properties of adsorbed monolayers play a role in determining how solid surfaces behave when in contact with one another. In biological systems, the adsorption of atoms and molecules onto the surface of a cell membrane is the first step in molecular recognition. See also: Electrochemistry; Heterogeneous catalysis; Molecular recognition

Because of the many important technological applications of adsorption, studies of adsorption are important in disciplines ranging from solid-state physics and physical chemistry to materials science and molecular biology. See also: Surface and interfacial chemistry; Surface physics

Brian E. Bent

How to cite this article

Please cite this article as follows:

Brian E. Bent, "Adsorption", in AccessScience@McGraw-Hill, http://www.accessscience.com /server-java/Arknoid/science/AS/Encyclopedia/0/01/Est_012100_frameset.html, last modified: July 24, 2001.

For Further Study

Topic Page: » Chemistry: » Physical chemistry

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1932
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Exhibit B

» **Physics:** » **Atomic and molecular physics**
» **Chemistry:** » **Physical chemistry**

Chemical bonding

The force that holds atoms together in molecules and solids. Chemical bonds are very strong. To break one in each molecule in a mole of material typically requires an energy of many tens of kilocalories.
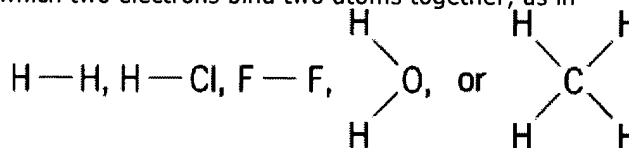
It is convenient to classify chemical bonding into several types, although all real cases are mixtures of these ide cases. The theory of the various bond types has been well developed and tested by theoretical chemists. See al: Computational chemistry; Molecular orbital theory; Quantum chemistry

The simplest chemical bonds to describe are those resulting from direct coulombic attractions between ions of opposite charge, as in most crystalline salts. These are termed ionic bonds. See also: Coulomb's law; Ionic crysi Structural chemistry

Other chemical bonds include a wide variety of types, ranging from the very weak van der Waals attractions, wh bind neon atoms together in solid neon, to metallic bonds or metallike bonds, in which very many electrons are spread over a lattice of positively charged atom cores and give rise to a stable configuration for those cores. Se(Crystal structure; Intermolecular forces

Covalent bond

But it is the normal covalent bond, in which two electrons bind two atoms together, as in

$$\text{H}\!-\!\text{H, H}\!-\!\text{Cl, F}\!-\!\text{F,} \quad \begin{array}{c}\text{H}\\ \diagdown\\ \diagup\quad\text{O, or}\\ \text{H}\end{array} \quad \begin{array}{c}\text{H}\qquad\text{H}\\ \diagdown\ \diagup\\ \text{C}\\ \diagup\ \diagdown\\ \text{H}\qquad\text{H}\end{array}$$

that is the most characteristic link in chemistry. The theory that accounts for it is a cornerstone of chemical scie The physical and chemical properties of any molecule are direct consequences of its particular detailed electroni structure. Yet the theory of any one covalent chemical bond, for example, the H—H bond in the hydrogen mole has much in common with the theory of any other covalent bond, for example, the O—H bond in the water mol The current theory of covalent bonds both treats their qualitative features and quantitatively accounts for the molecular properties which are a consequence of those features. The theory is a branch of quantum theory. See Nonrelativistic quantum theory ; Quantum chemistry

Hydrogen molecule

A brief outline of the application of quantum theory to the bond in the hydrogen molecule H—H follows. Here tw electrons, each of charge -e, bind together two protons, each of charge +e, with the electrons much lighter thar protons. What must be explained, above all else, is that these particles form an entity with the protons 0.074 nanometer apart, more stable by $D = 109$ kcal (456 kilojoules) per mole than two separate hydrogen atoms, wh is the binding energy. In more detail, a molecular energy is involved (ignoring nuclear kinetic energy) that depe internuclear distance, as shown in the illustration. This curve can be determined experimentally, and it can be u interpret the characteristic spectroscopic properties of hydrogen gas. See also: Molecular structure and spectra

Fig.   Potential energy of the hydrogen molecule.
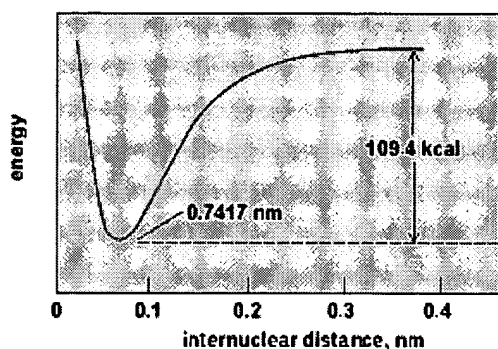
The quantum theory accounts for the properties of isolated atoms by assigning atomic orbitals for individual elec in, not more than two electrons at a time. For the hydrogen atom, the orbitals are labeled $1s$, $2s$., $2p_x$, $2p_y$, $2p_z$ with $1s$ the one having the lowest energy. For the molecule H_2 one electron, say electron 1, might be assigned t on proton A, with $1s_A(1)$ written to signify this; similarly electron 2 might be assigned to the same kind of orbita written as $1s_B(2)$. Since independent probabilities multiply and orbitals represent probability amplitudes, the des combined system shown in Eq. (1)

$$\phi(1,2) = 1s_A(1)1s_B(2)$$

is arrived at. Unfortunately, this fails to account for the bond properties; it gives a binding energy of only 10 kca mole. See also: Atomic structure and spectra; Exclusion principle

An essential defect of Eq. (1) is the numbering of the electrons; it puts electron 1 on proton A, electron 2 on pro Electrons cannot be distinguished experimentally, so they should not be given unique numbers; the function $1s_f$ would be just as good as the foregoing. It is necessary to use a description that is not affected by interchange o labels, as in the additive combination of Eq. (2).

$$\phi(1,2) = 1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)$$

(The difference combination also is an acceptable description, but it represents an excited state of the molecule.

Any complete molecular electronic wave function should include electron spin. Symmetric space wave functions must be multiplied by antisymmetric spin wave functions to give total wave functions that are antisymmetrical v interchange of electrons. For the ground state of hydrogen, and for the normal covalent bond elsewhere, this re means that the electron spins must be paired to give a total electron spin of zero.

The simple relationship described by Eq. (2) qualitatively accounts for the existence of the covalent bond; the pi energy is $D = 74$ kcal (310 kJ) per mole; and the shape of the curve, with the minimum appearing at 0.080 nm,

The description of Eq. (2) can be systematically improved. The charge acting on the electron may be changed fr larger value, $+Ze$, which is more realistic for the actual molecule. With $Z = 1.17$ this gives $D = 87$ kcal (364 kJ) Polarization effects may be introduced by taking Eq.

$$\phi(1,2) = 1\sigma_A(1)1\sigma_B(2) + 1\sigma_A(2)1\sigma_B(1)$$

(3), where $1\sigma_A = 1s_A + \lambda 2pz_A$ and $1\sigma_B = 1s_B + \lambda 2pz_B$. This gives $D = 93$ kcal (389 kJ). Ionic terms may be intro acknowledging the possibility that both electrons may be on one atom, by taking Eq. (4)

$$\phi(1,2) = C_1[1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)]$$
$$+ C_2[1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)]$$

where C represents a constant. This also gives (with $Z = 1.19$) $D = 93$ kcal (389 kJ). Another possible approach both ionic terms and polarization effects, and other terms involving $2s$, $3d$, $4f$, and other orbitals. If this is done obtains the observed D value and a potential curve that is in complete agreement with experiment.

The linear mixing of terms such as $1s_A(1)1s_B(2)$ is called resonance; the method of mixing covalent and ionic st called the valence bond (VB) method. The particular mixing coefficients can be found by the variational principle values for such parameters are those that make the total energy of the molecule, properly computed from quan a minimum. The energy expression contains only terms that have a direct classical interpretation: the kinetic en electrons, their energy of repulsion for one another, their energy of attraction for the nuclei, and the nuclear-nu energy. See also: Resonance (molecular structure)

Alternative descriptions of H_2 are possible, of which the most important is provided by the molecular orbital (MC

electrons are put one at a time into orbitals which are spread over the whole molecule, usually approximating th linear combinations of atomic orbitals (LCAO). For H_2 the lowest molecular orbital is $\phi_1 \approx 1s_A + 1s_B$, the next ϕ_2. The simplest molecular orbital description is displayed in

$$\phi(1,2) = \phi_1(1)\phi_2(2)$$

Eq. (5), which represents an equal weighting of covalent and ionic structures; it gives $D = 61$ kcal (255 kJ) for Z = 80 kcal (335 kJ) for $Z = 1.20$. More suitable is a mixture of this function with the function obtained by promot electrons from ϕ_1 to ϕ_2. The result of this configuration interaction process has the form of Eq. (6), and

$$\phi(1,2) = D_1\phi_1(2) + D_2\phi_2(1)\phi_2(2)$$

it is identical with the valence bond function of Eq. (4). In this manner more terms can be added, using more or again, the accurate potential energy curve is obtained.

The most accurate description known for the chemical bond in H_2 is a very complicated electronic wave function and observed values of D and other properties agree absolutely.

Complex molecules

The problem of the proper description of chemical bonds in molecules that are more complicated than H_2 has m difficulties. The qualitative theory of chemical bonding in complex molecules preserves the use of many chemica predate quantum chemistry itself; among these are electrostatic and steric factors, tautomerism, and electrone(quantitative theory is highly computational in nature and involves extensive use of computers and supercomput

The number of covalent bonds which an atom can form is called the covalence and is determined by the detaile(configuration of the atom. An extremely important case is that of carbon. In most of its compounds, carbon forr When these connect it to four other atoms, the directions of the bonds to these other atoms normally make ang 109° to one another, unless the attached atoms are crowded or constrained by other bonds. That is, covalent b(preferred directions. However, in accord with the idea that carbon forms four bonds, it is necessary to introduce double and triple bonds. Thus in the structural formula of ethylene, C_2H_4 (1), all lines denote
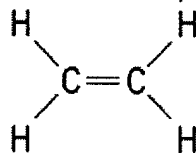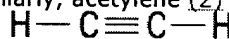

(1)
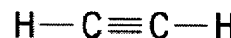
(2)

covalent bonds, the double line connecting the carbon atoms being a double bond. Such double bonds are distin almost twice as stiff, and require considerably more energy to break completely than do single bonds. However, require twice as much energy to break as a single bond. Similarly, acetylene (2) is

$$H-C\equiv C-H$$

(2)

written with a triple bond, which is still shorter than a double bond. A carbon-carbon single bond has a length cl 10-8 cm, whereas the triple bond is about 1.21 × 10-8 cm long. See also: Bond angle and distance; Valence

In many compounds the rules for writing bond formulas are not unique. For example, benzene, C_6H_6(3), can be forms. Evidence proves
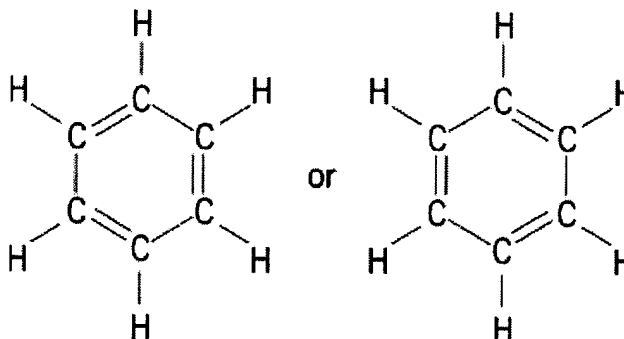
(3)

that all six C-C bonds are equivalent, so neither formula can be correct. The correct picture is a blend of the twc bonds have many properties intermediate between those of double and single bonds but in which the whole mol an additional stability. This resonance occurs whenever the structure is such that two or more different bond for

legitimately be drawn for the same geometry. See also: <u>Benzene</u>; <u>Electron configuration</u>

Many substances have some bonds which are covalent and others which are ionic. Thus in crystalline ammonium chloride, NH_4Cl, the hydrogens are bound to nitrogen by electron pairs, but the NH_4 group is a positive ion and the chlorine is a negative ion.

Both electrons of a covalent bond may come from one of the atoms. Such a bond is called a coordinate or dative covalent bond or semipolar double bond, and is one example of the combination of ionic and covalent bonding.

The hydrogen bond is a special bond in which a hydrogen atom links a pair of other atoms. The linked atoms are normally oxygen, fluorine, chlorine, or nitrogen. These four elements are all quite electronegative, a fact which favors a partially ionic interpretation of this kind of bonding. See also: <u>Electronegativity</u>; <u>Hydrogen bond</u>

To illustrate the level of accuracy of contemporary quantum-chemical calculations, the <u>table</u> gives observed and calculated values for certain spectroscopic properties of the H_2O molecule.

r_{OH} (E)†	

*After B. H. Besler et al., *J. Chem. Phys.*, 89:360, 1988. † E = 10^{-10} m.

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How to cite this article

Please cite this article as follows:

Robert G. Parr, "Chemical bonding", in <u>AccessScience@McGraw-Hill</u>, http://www.accessscience.com /server-java/Arknoid/science/AS/Encyclopedia/1/12/Est_126500_frameset.html, last modified: January 29, 2001.

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